

BNL-108250-2015-JA

**Real-time Observation of Morphological
Transformations in II-VI Semiconducting
Nanobelts via Environmental Transmission
Electron Microscopy**

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ABSTRACT

It has been observed that wurtzite II-VI semiconducting nanobelts transform into single-crystal, periodically branched nanostructures upon heating. The mechanism of this novel transformation has been elucidated by heating II-VI nanobelts in an environmental transmission electron microscope (ETEM) in oxidizing, reducing and inert atmospheres while observing their structural changes with high spatial resolution. The interplay of surface reconstruction of high-energy surfaces of the wurtzite phase and environment-dependent anisotropic chemical etching of certain crystal surfaces in the branching mechanism of nanobelts has been observed. Understanding of structural and chemical transformations of materials via in situ microscopy techniques and their role in designing new nanostructured materials is discussed.

Keywords: Nanotechnology, in-situ TEM, ETEM, heterostructure, nanobelt

Semiconducting nanostructures of varied morphologies have been widely studied for their useful physical properties leading to numerous potential applications ranging from electronics, photonics, energy conversion and storage to sensors¹⁻¹⁰. To realize their full potential, it is desirable to develop techniques that can also transform them into tunable and precisely controlled crystal structures and morphologies, which cannot be obtained during growth, and to understand the exact physical mechanisms behind such transformations¹¹⁻²¹. We report transformation of single-crystalline wurtzite (WZ) cadmium sulfide (CdS) and cadmium telluride (CdTe) nanobelts (NBs) into a periodically branched single-crystalline NB upon heating. To understand the atomistic details of the branching mechanism, we studied the

phenomenon in real-time in an environmental transmission electron microscope (ETEM) with high spatial resolution under different environmental conditions. The mechanism of branching is observed to be due to surface reconstruction of high-energy surfaces and environment-dependent anisotropic chemical etching of certain crystal surfaces. These studies, in addition to providing atomic level insights about the structural transformations in materials also underscores the importance of in situ microscopy techniques for characterization of complex materials phenomenon.

CdS NBs were synthesized via the vapor-liquid-solid (VLS) mechanism in a tube furnace set-up⁷ at 760 °C and were subsequently characterized for crystallography and chemical composition via TEM equipped with energy dispersive X-ray spectroscopy detector. All the measured NBs were single-crystalline and grew in the WZ crystal structure (Space group: $P6_3mc$), with a majority of them grown along the $\langle 1\bar{1}00 \rangle$ direction perpendicular to the c -axis $\langle 0001 \rangle$. Therefore, the samples are conventionally oriented along the $\langle 11\bar{2}0 \rangle$ zone-axis during TEM imaging (Figure 1 A). When CdS NBs were heated at 600 °C for 1 hour inside the same tube furnace (initially pumped down to moderate vacuum levels of ~25 mTorr) in an inert atmosphere (Argon), it is interesting to note that they transformed into branched nanostructures comprising of a central trunk from which nanoscale whiskers emanated in both directions, with a periodicity of tens of nanometers (Figure 1 B-C). TEM study of the new transformed morphology showed that the branched structures retained the crystallographic characteristics (single crystallinity and WZ crystal structure, Figure 1 D) and chemical composition (Figure S1) of the parent CdS NB. The most surprising aspect of this transformation is the presence of nano-whiskers (branches) at a periodic length scale pointing in the direction of c -axis along the entire length of the CdS NB. This morphological anisotropy and uniqueness warrants a deeper

investigation into the exact transformation mechanism. Therefore, to observe the morphological transformation process in CdS nanobelts in real-time, we performed in-situ heating experiments inside a conventional TEM under high vacuum (HV) at a base pressure of $\sim 10^{-7}$ Torr using the Gatan heating holder up to a temperature of 600 °C (ramping rate of 1 °C/sec). Upon heating the as-grown CdS NBs (Figure S2 A), we could only observe sublimation of the material occurring at different regions of the NB without any periodicity or correlation with each other, with the basal plane transforming into lower energy pyramidal planes (Figure S2 B). Sublimation typically initiated at the lateral edges, which then proceeded towards the core of the nanobelt, thereby increasing the surface area of the pyramidal planes at the cost of basal planes, eventually leading to the disappearance of the entire nanostructure.

Heating experiments inside a TEM under HV differs significantly from those performed inside the tube furnace owing to the differences in the pressure and composition of the two environments. Therefore, to replicate the tube furnace conditions, i.e., higher base pressure and real gaseous environments, and also observe the mechanism of morphological transformation of CdS NBs in real-time with high spatial resolution, measurements in an ETEM are required. ETEM, a unique and powerful experimental technique, allows real-time observation and detailed study of the morphological, chemical and structural evolution of crystalline structures under a variety of atmospheric conditions with high spatial resolution²²⁻²⁷.

We therefore heated CdS NBs inside the ETEM in different atmospheric conditions (see supplementary information for experimental details). Upon heating CdS NBs in an inert atmosphere (He ~ 0.16 Torr) up to 600 °C, only sublimation of the material was observed, similar to the results described for heating inside a HV TEM (Figure 2 A-C, Movie S1). Interestingly, upon repeating the ETEM experiment in an oxygen atmosphere (~ 0.16 Torr) at 500 °C, we

observed that the CdS NBs did transform into periodically branched nanostructures (Figure 2 D-F, Movie S2) similar to the results obtained from heating them in a tube furnace (Figure 1). We observed that the transformation process initiated from the basal plane (lateral surface of NBs) with the development of a periodic contrast along the growth axis of the NB $\langle 1\bar{1}00 \rangle$, which progressed inwards in the direction of the c-axis (Figure 2 E). These periodic contrasts due to the modulation in the thickness of the NB gradually disappear, leaving behind what appears as the final branched product (Figure 2 F). The in situ ETEM heating experiment was repeated in a hydrogen atmosphere (~ 0.16 Torr) and a similar morphological transformation as in the case of an oxidizing atmosphere (Figure 2 G-I, Movie S3) was observed. The only observable difference is the continuous carbon shell left behind on the transformed nanostructure which is a result of different reaction and different electron beam exposure conditions. These observations clearly demonstrate the role of a reactive atmosphere in the branching mechanism of the CdS NBs.

To further explore if the transformation to a branched structure occurs in other chemical systems upon heating NBs, we performed similar in-situ ETEM heating experiments in an oxygen atmosphere. CdTe NBs, synthesized via the VLS mechanism in a tube furnace set-up were obtained in both the WZ and zincblende (ZB) crystal structures (see supplementary information for experimental details). WZ CdTe NBs are identical to their CdS counterparts in terms of their crystallography, whereas ZB CdTe NBs (Space group: $F\bar{4}3m$) grow along the $\langle 112 \rangle$ direction, and their lateral surfaces are the polar $\{111\}$ high surface energy planes. Therefore, the top surface of ZB CdTe NBs are the non-polar lowest surface energy $\{110\}$ planes (Figure S3) ²⁸. In the ETEM heating experiments, we observed that WZ CdTe NBs undergo branching when heated up to 500 °C (Figure 3 A-C, Movie S4), similar to WZ CdS NBs, whereas ZB NBs sublime around 600 °C without any branching (Figure 3 D-F, Movie

S5). Some of the CdTe NBs naturally form heterostructures with the ZB structure in the center and WZ structure towards the lateral edges; in situ heating these materials (until 600 °C) under an oxidizing atmosphere displayed branching only in the WZ region and sublimation in the ZB region (Figure 3 G-I, Movie S6). These observations establish that the morphological transformation process is dependent on the crystal structure of the material besides temperature and atmospheric conditions.

Based on these observations, a mechanism for the branching phenomenon is proposed. The branching mechanism is essentially a chemical etching process in a reactive atmosphere that proceeds only along preferential crystallographic planes thereby resulting in a highly anisotropic morphological transformation. It is well known that the basal planes of polar compounds such as II-VI semiconductors have the highest surface energy in spite of being closed packed due to their polar nature (presence of only Cd^{2+} or S^{2-} atoms), and therefore the system tries to reduce its free energy by minimizing the surface area of these planes during crystal growth^{29, 30}. Therefore in CdS NBs, the high surface energy basal plane, either entirely or to a large extent, often rearranges to form lower surface energy vicinal planes of the pyramidal type while the lowest surface energy top surface (non-polar prismatic plane) remains smooth^{31, 32}. This was confirmed via scanning electron microscopy (SEM) and atomic force microscopy (AFM) of the lateral surfaces, which show that either the entire basal plane or a large fraction of it consists of vicinal surfaces with a periodicity of tens of nanometers (Figure 4A), similar to the periodicity of the observed branches in the transformed structure. Therefore, the presence of these periodic vicinal surfaces is instrumental in the branching process since they provide a template for the chemical etching process to initiate while retaining the original periodicity in the transformed nanostructure.

For the chemical etching process of the NBs, the etchant is either oxygen or hydrogen gas that reacts with CdS at elevated temperatures, which leads to controlled sublimation of the NB material. Periodic vicinal planes, present only on the lateral edges of as-grown WZ NBs, provide a nucleation site for the etching process to initiate (Figure 4B). The initial etching should take place on the remainder of the basal plane owing to its high surface energy and chemical reactivity and convert it into vicinal surfaces (Figure 4B). The etching reaction may also initiate at high-energy planar defects such as stacking faults and twin boundaries, which are often present in II-VI semiconducting materials, especially WZ/ZB heterostructured materials. This can be observed in Movie S6 where etching is simultaneously initiated at stacking faults at the WZ/ZB interface in addition to the lateral surface of the nanobelt. However, this etching process lacks periodicity observed at the lateral surface since the defect plane is a continuous surface and not corrugated. The reaction should then proceed at the vicinal planes and the top surface, especially at the edges where the two meet creating notches (Figure 4C). The notches will expose the other set of low surface energy prismatic planes that are parallel to the c -axis, thereby dictating the anisotropy in the process and ensuring that further etching occurs only along the c -axis. This step is also important since the periodicity of the final product is determined by the periodicity of the notches created at the edge, which in turn is dependent on the initial periodicity of the vicinal planes. Further etching of the top surface, initiated at the notches, along the c -axis leads to a periodic thickness modulation observed as a thickness contrast (Figure 4D). Once this thinnest part of the NB is completely etched, we are left with the periodically branched NB structures (Figure 4E). Inside our tube furnace set-up, which can be pumped at most to a base pressure is ~ 25 mTorr, there is enough residual partial pressure of oxygen to cause etching of the NBs. On heating WZ NBs in HV or an inert atmosphere inside ETEM, where the base pressure

($\sim 10^{-7}$ Torr) reduces the residual oxygen to a negligible level, only sublimation (without any chemical etching) occurs at high temperatures (~ 600 °C) due to the lack of any etching agents. As observed in our experiments, high temperature sublimation does not necessarily follow the periodicity of the vicinal planes or other crystallographic directions owing to higher sublimation rates such that the vicinal planes sublime and merge to form large voids even before periodic notch formation can be initiated (Figure S2) and therefore doesn't lead to the formation of periodically branched NBs. Zincblende CdTe NBs fail to exhibit branching mechanism for several key reasons; the lateral surfaces of ZB NBs are polar high energy $\{111\}$ surfaces, which may not reconfigure into vicinal planes since one of the resulting vicinal surface will be another high energy $\{100\}$ polar surface²⁸. Another important factor is that the top surface of the ZB NB is the non-polar low energy $\{110\}$ surface: upon etching, this surface will tend to reconfigure into another set of $\{110\}$ low surface energy planes. However, unlike the case of the low symmetry WZ crystal structure, these planes will not always be parallel to the $[111]$ direction and therefore the etching mechanism loses directionality leading to only random sublimation (Figure S4).

To further confirm our hypothesis, a control experiment was devised to understand the role of vicinal surfaces and subsequent notch formation in the branching mechanism. As-grown WZ CdS nanobelts were heated to 550 °C in a tube furnace under ambient conditions for only 10 minutes since the purpose of the experiment was to initiate and arrest the branching process in its nascent stage for analysis. Characterization of these partially transformed structures in SEM showed that the NBs displayed well-defined vicinal planes on the lateral surface and the beginning of the development of notches along with periodic corrugations on the top surface, which confirm the role of these vicinal surfaces in the directional etching process leading to

branching (Figure 5 A-B). These NBs were then heated under HV inside a regular HV TEM to ~500 °C. Unlike the earlier experiments, where as-grown CdS NBs upon heating in-situ under HV sublime randomly, pre-notched CdS NBs now transformed into periodic branches (Figure 5C-E, Movie S7), although not as well defined as the ones observed in ETEM experiments owing to a higher sublimation rate in HV TEM, which competes with the etching process. This observation illustrates the importance of the onset of the directional etching process on the top surface of the NBs, which dictates the subsequent morphological transition, and the absence of which leads to only random sublimation of the material.

In conclusion, we have succeeded in observing in real-time a complex morphological transformation by using a powerful technique such as the ETEM under various experimental conditions in II-VI NBs. Upon heating II-VI semiconducting NBs in a variety of environmental conditions, we observe a controlled chemical etching process which retains the original periodicity of the WZ vicinal surfaces leading to the formation of a periodically branched nanostructure. In addition to obtaining new insights into the atomistic mechanism of morphological transformations of nanostructures, a simple route to engineer novel morphologies at the nanoscale has been realized. Based on these insights, new morphologies can be obtained in nanostructures, which can be utilized for a variety of electronic, photonic and sensing devices.

References

1. Agarwal, R.; Lieber, C. M. *Appl. Phys. A* **2006**, 85, (3), 209.
2. Wei, B. Q.; Vajtai, R.; Jung, Y.; Ward, J.; Zhang, R.; Ramanath, G.; Ajayan, P. M. *Nature* **2002**, 416, (6880), 495.
3. Hayden, O.; Agarwal, R.; Lieber, C. M. *Nat. Mater.* **2006**, 5, (5), 352.
4. Lieber, C. M. *MRS Bull.* **2003**, 28, (7), 486.
5. Piccione, B.; Agarwal, R.; Jung, Y.; Agarwal, R. *Philos. Mag.* **2013**, 93, (17), 2089.
6. Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, Y. Q. *Adv. Mater.* **2003**, 15, (5), 353.
7. Piccione, B.; van Vugt, L. K.; Agarwal, R. *Nano Lett.* **2010**, 10, (6), 2251.
8. Thelander, C.; Agarwal, P.; Brongersma, S.; Eymery, J.; Feiner, L. F.; Forchel, A.; Scheffler, M.; Riess, W.; Ohlsson, B. J.; Gosele, U.; Samuelson, L. *Mater. Today* **2006**, 9, (10), 28.
9. Agarwal, R. *Small* **2008**, 4, (11), 1872.
10. Nukala, P.; Agarwal, R.; Qian, X. F.; Jang, M. H.; Dhara, S.; Kumar, K.; Johnson, A. T. C.; Li, J.; Agarwal, R. *Nano Lett.* **2014**, 14, (4), 2201.
11. Jung, Y.; Ko, D. K.; Agarwal, R. *Nano Lett.* **2007**, 7, (2), 264.
12. Herman, I.; Yeo, J.; Hong, S.; Lee, D.; Nam, K. H.; Choi, J. H.; Hong, W. H.; Lee, D.; Grigoropoulos, C. P.; Ko, S. H. *Nanotechnology* **2012**, 23, (19).
13. Zhang, B.; Jung, Y.; Chung, H. S.; Van Vugt, L.; Agarwal, R. *Nano Lett.* **2010**, 10, (1), 149.
14. Dick, K. A.; Deppert, K.; Larsson, M. W.; Martensson, T.; Seifert, W.; Wallenberg, L. R.; Samuelson, L. *Nat. Mater.* **2004**, 3, (6), 380.
15. Pradhan, D.; Sharon, M.; Kumar, M.; Ando, Y. *J. Nanosci. Nanotechnol.* **2003**, 3, (3), 215.
16. Bierman, M. J.; Jin, S. *Energy Environ. Sci.* **2009**, 2, (10), 1050.
17. Ting, J. M.; Chang, C. C. *Appl. Phys. Lett.* **2002**, 80, (2), 324.
18. Qiu, Y. C.; Yan, K. Y.; Deng, H.; Yang, S. H. *Nano Lett.* **2012**, 12, (1), 407.
19. Kuznetsov, D. K.; Shur, V. Y.; Negashev, S. A.; Lobov, A. I.; Pelegov, D. V.; Shishkin, E. I.; Zelenovskiy, P. S.; Platonov, V. V.; Ivanov, M. G.; Osipov, V. V. *Ferroelectrics* **2008**, 373, 133.
20. Numao, S.; Judai, K.; Nishijo, J.; Mizuuchi, K.; Nishi, N. *Carbon* **2009**, 47, (1), 306.
21. Yu, H. D.; Wang, D.; Han, M. Y. *Adv. Mater.* **2008**, 20, (12), 2276.
22. Cargnello, M.; Doan-Nguyen, V. V. T.; Gordon, T. R.; Diaz, R. E.; Stach, E. A.; Gorte, R. J.; Fornasiero, P.; Murray, C. B. *Science* **2013**, 341, (6147), 771.
23. Fujita, T.; Guan, P. F.; McKenna, K.; Lang, X. Y.; Hirata, A.; Zhang, L.; Tokunaga, T.; Arai, S.; Yamamoto, Y.; Tanaka, N.; Ishikawa, Y.; Asao, N.; Yamamoto, Y.; Erlebacher, J.; Chen, M. W. *Nat. Mater.* **2012**, 11, (9), 775.
24. Yoshida, H.; Kuwauchi, Y.; Jinschek, J. R.; Sun, K. J.; Tanaka, S.; Kohyama, M.; Shimada, S.; Haruta, M.; Takeda, S. *Science* **2012**, 335, (6066), 317.
25. Tao, F.; Salmeron, M. *Science* **2011**, 331, (6014), 171.
26. Kim, S. M.; Pint, C. L.; Amama, P. B.; Zakharov, D. N.; Hauge, R. H.; Maruyama, B.; Stach, E. A. *J. Phys. Chem. Lett.* **2010**, 1, (6), 918.
27. Stach, E. A.; Pauzuskie, P. J.; Kuykendall, T.; Goldberger, J.; He, R. R.; Yang, P. D. *Nano Lett.* **2003**, 3, (6), 867.
28. Wright, K.; Watson, G. W.; Parker, S. C.; Vaughan, D. J. *Am. Mineral.* **1998**, 83, (1-2), 141.
29. Ballentyne, D. W. G.; Rouse, L. M. *J. Cryst. Growth* **1977**, 39, (2), 231.
30. Manna, L.; Wang, L. W.; Cingolani, R.; Alivisatos, A. P. *J. Phys. Chem. B* **2005**, 109, (13), 6183.
31. Ma, C.; Ding, Y.; Moore, D.; Wang, X.; Wang, Z. L. *J. Am. Chem. Soc.* **2003**, 126, (3), 708.

32. Ibach, H.; Emma Louise McClellan Fund., *Physics of surfaces and interfaces*. Springer: Berlin ; New York, 2006; p xii.

Acknowledgements: This work was supported by XXX. SEM and regular TEM electron microscopy experiments were performed at the Singh Center for Nanotechnology at the University of Pennsylvania. Environmental TEM experiments were performed at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704.

Supplementary information

SEM, TEM and ETEM Experimental Details, Growth Details of CdTe Nanobelts

Figures S1-S4

Captions for Movies S1 to S7

Videos S1 to S7

Figure Captions:

Figure 1: Structural characterization of branched CdS nanostructures obtained by heating CdS nanobelts in moderate vacuum. A) Transmission Electron Microscope image of an as-grown wurtzite CdS nanobelt growing perpendicular to the c-axis. Inset: selected area electron diffraction (SAED) pattern of the nanobelt. Scale bar: 200 nm B) and C) TEM images of two periodically branched nanobelts obtained by heating CdS nanobelts inside a tube furnace (pumped down to moderate base pressure of ~25 mTorr) at 600 °C under Argon flow (100 Torr at 15 sccm). Scale bar: 200 nm D) High-resolution TEM micrograph of the branched region confirming retention of single crystallinity and crystal orientation of the entire structure after the morphological transformation. Scale bar: 5 nm.

Figure 2: Real-time observation of morphological transformation in wurtzite CdS nanobelts upon heating in environmental TEM under various atmospheric conditions. A) - C) Snapshots from Movie S1 showing real-time sublimation but no branching in a wurtzite CdS nanobelt in the presence of inert helium (0.16 Torr) inside an environmental TEM upon heating to a temperature of 600 °C. Inset: SAED pattern of the nanobelt. Scale bar: 200 nm D) - F) Snapshots from Movie S2 showing real-time branching of a wurtzite CdS nanobelt in the presence of oxygen (0.16 Torr) inside an environmental TEM at 500 °C. Inset: SAED pattern of the nanobelt. Scale bar: 100 nm G) - I) Snapshots from Movie S3 showing real-time branch formation in a wurtzite CdS nanobelt in the presence of hydrogen (0.16 Torr) inside an environmental TEM at 500 °C. Inset: SAED pattern of the nanobelt. Scale bar: 100 nm

Figure 3: Real-time observation of morphological transformation in wurtzite and zincblende CdTe nanobelts upon heating in environmental TEM under various atmospheric conditions A) - C) Snapshots from Movie S4 showing real-time branching of a wurtzite CdTe nanobelt in the presence of oxygen (0.16 Torr) inside an environmental TEM at 500 °C. Inset: SAED pattern of the nanobelt. D) - F) Snapshots from Movie S5 showing real-time sublimation but no branching of a zincblende CdTe nanobelt in the presence of oxygen (0.16 Torr) inside an environmental TEM up to 600 °C. Inset: SAED pattern of the nanobelt. G) – I) Snapshots from Movie S6 showing real-time branching and sublimation of a CdTe nanobelt in the presence of oxygen (0.16 Torr) inside an environmental TEM at 600 °C. The nanobelt contains both zincblende and wurtzite phases and branching is only observed in the wurtzite phase while sublimation is observed in the zincblende phase. Inset: SAED pattern of the nanobelt.

Figure 4: Schematic of the branching mechanism in II-VI wurtzite nanobelts. A) SEM micrograph of an as-grown CdS nanobelt clearly displaying periodic vicinal surfaces along the basal plane. Inset: AFM micrograph of a nanobelt displaying periodic vicinal surfaces. B) Schematic of an as grown wurtzite CdS nanobelt with periodic vicinal planes (exaggerated for clarity) along the basal plane. C) Subsequent etching of the prismatic planes (top surface) of the nanobelt owing to oxidation/reduction (depending on the environmental conditions) leading to periodic thickness variation along the length of the nanobelt. D) Further etching into both the prismatic and basal planes leads to periodic thickness contrasts in the nanobelt. E) Complete

etching of the thinner regions leaves behind the relatively thicker parts in CdS nanobelts, leading to the formation of periodically branched nanostructures.

Figure 5: A control experiment comprising of ex-situ heating of CdS nanobelts in a tube furnace at moderate vacuum levels followed by in situ TEM heating under HV. A) – B) SEM micrograph of wurtzite CdS nanobelts after heating in a tube furnace for 10 minutes at 550 °C (base pressure 25 mTorr). Evolution of the etched surfaces on both the basal and prismatic planes can be clearly observed leading to the formation of notches. C) – E) Snapshots from Movie S7 showing real-time branch formation in a pre-notched wurtzite CdS nanobelt, whose long axis is at an angle of 105° with respect to *c-axis*, upon heating inside a conventional TEM under UHV at 500 °C. Inset: SAED pattern of the nanobelt confirming the crystal structure and growth direction.